

BLAST FURNACE TESTS WITH COKES OF DIFFERING REACTIVITY

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Pig iron is produced in blast furnaces by heating and reducing iron ore with furnace coke and products of combustion. Combustion and gasification of the coke near the bottom of the furnace provide the required temperatures and reducing atmosphere. This paper deals with coke savings observed on commercial blast furnaces when petroleum coke was added to the coal blend before carbonizing in by-product ovens. An analysis of the furnace operating results indicate that changes in coke structure which affect reactivity were responsible for reduction in coke rate.

HISTORY

Blakley and Cobb (1) in England, and Broche and Nadelman (2) in Germany, are typical of many investigators who have speculated for many years on desirable coke characteristics for blast furnace use. They concluded that a coke arriving at the tuyeres in larger proportions was desirable. To attain this, the gasification of coke carbon further up the shaft must be reduced. This gasification is called "solution loss" which involves the reaction of coke carbon with carbon dioxide originating from indirect reduction of iron oxides and calcination of carbonates.

Our experience with special foundry coke indicates that a furnace coke less reactive to gasification in the upper and cooler portion of the furnace can be produced. A coke of this type contains less internal pore surface and thicker cell walls. When used in cupolas, a coke reduction is experienced, in addition to use of more air per pound of coke charged, higher combustion temperatures, and higher concentration of carbon dioxide in the off-gas. The increased carbon dioxide concentration indicates that the reaction of coke carbon with carbon dioxide can be depressed in cupolas. Thus, if the same can be accomplished in a blast furnace, the "solution loss" would be reduced.

The practical advantage experienced by the use of special foundry coke in cupolas led to the idea that blast furnace coke could similarly be improved. Hence, plant scale blast furnace tests were planned.

PRELIMINARY PLANT TESTS AT OBERSCHELD, GERMANY

A one month test, with a low internal surface dense foundry coke, was made in a small blast furnace producing foundry pig iron at Hessische Berg-Und Huttenwerke, Oberscheld, Germany. In this test various proportions of normal furnace coke were replaced with dense H-C Coke, a special foundry coke. This coke was produced by Verkaufs Vereinigung Fur Teererzeugnisse who operate under a license agreement with Great Lakes Carbon Corporation.

Table I summarizes the results of a 166-hour test on the Oberscheld blast furnace in which 33.4 percent H-C Coke was substituted for normal coke. The data show the average practice for normal coke and for a mixture of 2/3 normal coke and 1/3 of H-C Coke.

The replacement of 33.4 percent normal coke by H-C Coke was accompanied by an increase in silicon and a reduction of sulphur in the hot metal, reflecting increased hearth temperatures. As a result, the operator chose the following changes in practice while producing iron of comparable sulfur content :

- 1) Coke rate reduction of 44 pounds per ton of hot metal
- 2) Blast temperature reduction of 144°F
- 3) Increase in hard to reduce ore of 174 pounds per ton of hot metal
- 4) Reduction of scrap iron of 192 pounds per ton of hot metal
- 5) Reduction in stone rate of 138 pounds per ton of hot metal with equal slag volume at a basicity reduction from 1.40 to 0.95.

TABLE NO. I

H-C COKE PERFORMANCE VS NORMAL COKE
OBERSCHELD BLAST FURNACE TEST II
 (Working Volume - 7230 Cu. Ft.)

<u>TEST CONDITIONS</u>	<u>NORMAL COKE</u> <u>(28 Days)</u>	<u>H-C COKE MIX</u> <u>(166 Hours)</u>
<u>FURNACE COKE</u>		
Normal Coke, %	100 Days	66.6
H-C Coke, %	-	33.4
<u>COKE ANALYSIS</u>		
Ash, %	8.7	7.2
Sulfur, %	0.92	0.97
<u>FURNACE CHARGE</u>		
Pounds Coke/THM (As charged)	1860	1816
Pounds Stone/THM	384	246
Ore, % Fe	40.2	41.7
Pounds Scrap Iron/THM	426	234
Pounds Hard To Reduce Ore/THM	224	398
Pounds Oxygen in Ore/THM	618	732
<u>PRODUCTION</u>		
Tons Hot Metal Per Day	167.0	173.6
Hot Metal, % Silicon	3.22	2.93
% Sulfur	0.016	0.021
Slag Volume, Pounds/THM	1338	1342
Slag Basicity, Base/Silica and Alumina	1.40	0.95
Off Gas, % Carbon Dioxide	8.2	9.1
% Carbon Monoxide	32.3	31.5
% Hydrogen	2.4	2.0
% Nitrogen	57.1	57.4
<u>OPERATING CONDITIONS</u>		
Blast Temperature, °F	1526	1382
Blast Pressure, PSIG	9.38	9.41
Wind Delivered, CFM	10430	10400

It was difficult to evaluate the results given in Table I in respect to coke savings by the use of H-C Coke as the burden used during the test period differed considerably from the one normally used. During the test period on H-C Coke 398 pounds of so called hard to reduce ore were used per ton of hot metal compared with 224 pounds during the base period. With normal practice it was reported an excess of 250 pounds or hard to reduce ore results in cold iron at Oberscheld. The significance of an increase of 174 pounds of ore per ton of hot metal cannot be fully appreciated unless it is pointed out that extremely dense Kiruna D, Swedish Magnetite, was charged in 4-6 inch lumps. Such ores would tend to contribute to carbon dioxide at low levels in the blast furnace and result in more solution loss. A reduction in the scrap per ton of hot metal from 426 pounds in the base period to 234 pounds in the test period is also significant because an additional amount of iron had to be reduced from ore.

In order to obtain a better understanding of coke saving, the practice values obtained were evaluated with the use of the Flint Coke Rate Formula (3) (4) which corrects for burden and iron analysis variations. The results thus calculated are shown on Graph No. I. The significance of this Graph was that a calculated coke saving occurred and increased linearly with H-C Coke replacement of normal furnace coke. Of special importance was the excellent correlation of the results with variation of percentages of H-C Coke used from which it was concluded that the data obtained are reliable. This conclusion ultimately led to the development of a special furnace coke.

TABLE NO. II

RESULTS OF H-C COKE REACTIVITY
OBERSCHELD TEST II

<u>OPERATING VARIABLES</u>	<u>CHANGE IN PRACTICE VALUE</u>
Coke Reduction, pounds/THM	87 (a)
Blast Temp. Reduction °F	144
Stone Reduction, Pounds/THM	138
Slag Basicity Reduction, Base/Silica and Alumina	0.45
CO ₂ , Increase in Off-Gas, %	0.9

(a) Corrected for burden variation with Flint Coke Rate Formula.

Table No. II. shows that the preliminary Oberscheld blast furnace tests with special foundry coke resulted in reduced coke rate, reduced stone usage and in increased carbon dioxide content in the off-gas. Of special interest is the fact that normal desulfurization was obtained despite the reduction of 0.45 slag basicity from 1.40 to 0.95 at equivalent slag volume and slag sulfur content. (1.3). These findings were anticipated from our cupola experience with dense foundry coke.

DEVELOPMENT OF P-C COKE

Before making further blast furnace tests a special low cost furnace coke was developed simulating the useful reactivity characteristics displayed by 33.4 percent H-C Coke mixtures with normal furnace coke. This coke, called P-C Coke, was manufactured in normal by-product ovens and was produced from coal blends containing appropriately sized petroleum coke. A three (3) month and a one (1) month plant scale blast furnace test were made with this coke at two (2) large steel plants in the States.

COOPERATIVE COLORADO FUEL AND IRON CORPORATION TESTS

The initial use of P-C Coke in a blast furnace was made at the Pueblo Plant of The Colorado Fuel and Iron Corporation. This coke was produced from their normal high volatile coals and the replacement of low volatile coals with minus 1/8 inch petroleum coke furnished by Great Lakes Carbon Corporation. Petroleum coke is the residue obtained from coking residual petroleum oil.

TABLE NO. III

P-C COKE PERFORMANCE VS REGULAR COKE
CF&I THREE MONTH PLANT TEST

(Hearth Dia., 20 Ft., 3 In., Working Vol., 26015 Cu. Ft.)

<u>TEST CONDITIONS</u>	<u>REGULAR COKE</u>	<u>P-C COKE</u>	
	<u>BASE PERIOD</u>	<u>AVERAGE</u>	<u>AVERAGE(a)</u>
<u>COKE ANALYSIS</u>	<u>(158 Days)</u>	<u>(85 Days)</u>	<u>(23 Days)</u>
Ash, %	11.6	11.8(b)	11.8(b)
Sulfur, %	0.57	0.63	0.61
<u>FURNACE CHARGE</u>			
Pounds Coke/THM (As charged)	1514	1414	1350
Pounds Stone/THM	605	547	509
Theoretical Pig Yield, %	53.3	52.8	53.6
<u>PRODUCTION</u>			
Tons Hot Metal Per Day	651	655	709
Hot Metal, % Silicon	1.13	1.10	1.08
Hot Metal, % Sulfur	0.044	0.045	0.047
<u>OPERATING CONDITIONS</u>			
Blast Temperatures, °F	1075	981	1000
Blast Pressure, PSIG	19.9	21.5	21.4
Wind Delivered, CFM	35560	34410	35320

Note (a) Snowfall 0.1" water compared to normal of 0.03".

Note (b) Problems in Washery caused coal ash increase. Petroleum coke contains 0.3 percent Ash.

Table III summarizes the results of a three (3) month blast furnace P-C Coke test in comparison with normal practice. The data shown in Table III represent the average values obtained. It is to be noted that the information was gathered from operating records. The values appearing in the last column under the heading "Average" (23-day) represent a 23 day, consecutive period included in the 85 day test run. A review of Table III indicated the following :

1. Hearth Temperature Increase - Visual inspection of the tuyeres, at the time, when P-C Coke first reached the hearth, showed an increase in temperature. An increase in the percent of silicon and a reduction in sulfur in the hot metal produced also reflected an increase in hearth temperature. This increase in hearth temperature permitted, and in fact required, changes in practice to produce hot metal of the usual analysis.

Average changes in practice for the 85 day period on P-C Coke follows :

1. Coke rate reduced 100 pounds.
2. Stone rate reduced by 58 pounds.
3. Blast temperature reduced by 94° F.

Inasmuch as the carbon content of the coke remained essentially constant a reduction of this order of magnitude in the coke rate indicates that more heat was obtained from each pound of P-C Coke charged. This follows because the heat required per ton of iron did not change significantly as the chemical and physical character of the burden remained fairly constant.

2. Solution Loss - A reduction in solution loss is indicated by the use of more air (1.8 cubic feet) per pound of P-C Coke charged, despite a reduction of 2620 cubic feet of wind per ton hot metal. This shows that a larger percentage of the coke reaches the tuyeres and less of it was gasified above the tuyeres. The reduction in gasification above the tuyeres is attributed to the lower reactivity of the P-C Coke towards carbon dioxide. The twofold effect of decreasing solution loss and bringing more carbon to the tuyeres is larger than one might at first anticipate.

For simplicity it will be assumed that solution loss of carbon is decreased by 48 pounds or 4 pound mols per ton hot metal.

HEAT EFFECTS OF REDUCING SOLUTION LOSS

Heat Loss due to Solution Loss	$4C + 4 CO_2$	= 8 CO	296,780 BTU
Heat Gain due to Combustion	$4C + 2O_2$	= 4 CO	<u>190,200 BTU</u>
Additional Heat Available			486,980 BTU

Thus from the above tabulation it can be seen that a reduction in solution loss of 50 pounds increases the available heat by about 500,000 BTU per ton of hot metal.

3. Blast Temperature - Because the furnace was a little tighter the operators chose to operate with a 94°F lower blast temperature on P-C Coke. By improving the physical character of the burden (such as pellets, etc.,) so as to reduce blast pressure, a still further improvement in coke rate would have been possible by keeping the blast temperature closer to normal levels. As an alternate some 3 to 4 grains of moisture could have been added to the blast to obtain a faster rate of driving and more tonnage. The effect of blast humidity is manifest in the 23 day period when the average rainfall (snow) was above normal. Hot metal tonnage and coke rates were more favorable during this period as shown in Table III.
4. Blast Pressure - The slight tightening of the furnace with P-C Coke resulting in a blast pressure increase of 1.6 pounds was, in the main, ascribed to a reduction of the volume of the raceway. The reasoning for this was that the conditions appeared similar to those experienced by others with increased blast temperature (5) or oxygen enrichment (6). Credence to this hypothesis was further given by the practice in the 23 day period resulting in normal wind rates and 9 percent capacity increase with a 164 pound coke reduction. The increased coke rate reduction shows the potentials that exist with improved practice such as increased humidity in blast and better gas solid contact.

Further, foundry experience with dense coke leads to the theory that the maximum carbon dioxide concentration in the combustion zone with P-C Coke is higher and located closer to the tuyeres than with normal coke. A condition of this type would explain the tightening of the furnace and loosening with steam.

OPERATING VARIABLES CHANGED BY USE OF P-C COKE

Table IV summarizes the change in practice values attributed, in the main, to improved useful coke reactivity. To some extent the reduction in coke rate was also contributed to by the increase of 11.0 to 14.2 percent in the iron concentration in the charge caused by a reduced coke and lime volume in the 85 and 23 day periods respectively. The increase in air requirement per pound of coke charged and reduction in air required per ton of hot metal is in agreement with our dense foundry coke experience in cupolas and is significant.

Manes and Mackay (7) with thermal and equilibrium data, constructed a simplified model of a blast furnace to derive a quantitative estimate of coke rate. They show a coke saving results from an increase in air per pound of coke charged with concomitant reduction in air per ton hot metal. This is the same finding as found in the CF&I test.

TABLE IV.RESULT OF P-C COKE REACTIVITY
CF&I THREE MONTH PLANT TEST

<u>OPERATING VARIABLES</u>	<u>CHANGE IN</u>	
	<u>PRACTICE VALUE</u>	
	<u>AVERAGE</u> <u>(85 Days)</u>	<u>AVERAGE</u> <u>(23 Days)</u>
More-Air/Pound Coke Chg., Cu. Ft.	1.8	1.5
Less Air/THM, Cu. Ft.	2620	6450
Less Coke/THM, Pounds	100	164
Less Blast Temp. °F	94	75
Less Stone/THM, Pounds	58	96
Increase in Daily Metal Production, %	0.6	8.9

P-C COKE STRUCTURE

Before reviewing the reducing and temperature conditions in a blast furnace as related to fundamentals of coke gasifications, the significant structural characteristics of P-C Coke are discussed. Of special importance are those P-C Coke characteristics which affect its rate of gasification at various temperatures experienced in a blast furnace.

The physical coke characteristics relating to gasification are significantly affected by inclusion of petroleum coke in the coal blend when producing P-C furnace coke. These become readily apparent when viewed under a microscope.

The effect of replacement of low volatile coal with petroleum coke in a given blast furnace coal blend is shown in Figures 1 and 2 at 10X magnification. In Figure 1 the normal blast furnace coke produced with low volatile coals is shown. The black portions are the pores filled with a black resin while the light portions are the cell walls. The specimen before photographing requires a high degree of polish. In this operation, great care was exercised so that some of the fragile extremely thin cell walls are not in part destroyed. Normal furnace coke in Figure 1 at 10X magnification gives the appearance of discontinuity of some of the fine white cell walls. When this is viewed under a microscope at 40X magnification the continuity of the cell walls can be observed. It is, however, to be noted that in Figure 4 at 40X magnification the discontinuity of the fine cell walls is again noted. The reason for this is the lack of photographic sensitivity with the bright lighting required. This type of lighting is required for accentuating the petroleum coke highlights and was used for all photographs. When keeping this in mind it is noted that the normal furnace coke shows a larger number of relatively small pores with considerable thin cell walls as compared to P-C Coke shown in Figure 2. Further comparing the 10X magnification of normal and P-C Coke it is noted that P-C Coke has larger pores.

In Figure 2, attention is called to the amorphous-appearing white highlights in the cell walls. These highlights are petroleum coke particles which are firmly bonded into carbonized coal matrix. Close inspection as shown by 40X magnification of P-C Coke in Figure 3 also reveals that larger particles of petroleum coke are tightly bonded into the matrix and that fine petroleum coke particles are included in the cell walls thus contributing to their thickness. For comparison purposes Figure 4 shows a 40X magnification of normal furnace coke. This again shows in comparison to Figure 3 that the cell walls in P-C Coke are massive and thick. In order to observe the effect of low volatile coal in the normal furnace blend, a coke was produced in a commercial oven without the use of low volatile coal in the high volatile coal blend. The coke thus produced is shown in Figure 5 at 40X magnification. An inspection shows that even thinner cell walls resulted with the removal of low volatile coal from the normal furnace coke blend. Therefore, the thicker cell walls in P-C Coke are not attributed to the removal of low volatile coal from the blend, but rather to its replacement with petroleum coke. To accomplish this the petroleum coke must have altered the coalescence of the plastic coal in such a manner as to produce thicker cell walls in the P-C Coke.

That petroleum coke contributes to the coalescence of cell walls at first may seem surprising as it does not become plastic in the same manner as bituminous coking coals on heating. In order to assist in clarification of this property, petroleum coke was macroscopically inspected before and after carbonization. Figure 6 shows a 10X magnification of petroleum coke before carbonization. The black portions are the pores filled with a black resin and the light portion represents the cell walls. Of interest are the black lines traversing the cell walls. These lines are thermal shrinkage cracks and on carbonization result in structural weakness in the P-C Coke produced. In order to eliminate this weakness, petroleum coke must be precrushed to about 90 percent or more minus 1/8 inch in size, before inclusion in the coal blend. An impact type mill has been found quite satisfactory for this purpose.

On carbonization of petroleum coke the thermal shrinkage cracks are accentuated as illustrated in Figure 7. These fissures, of course, can be substantially eliminated by precrushing. The amorphous appearing cell walls are bordered by a darker appearing homogeneous mass. This is the carbonization product of the heavier volatile content of the petroleum coke as it was expelled thermally from the internal portion of the petroleum coke. At one point of the thermal treatment during carbonization this material was plastic. This plastic portion of petroleum coke is not visible in P-C Coke. It was therefore concluded that it is diffused with the plastic material from the coal contributing to both bonding and coalescence of the cell walls.

However, as the plastic mass is limited, petroleum coke does not exhibit the bonding characteristics on heating typical of bituminous coking coals. This may explain why a more thorough blending with petroleum coke is desirable for higher tumbler values. From the macroscopic analysis it was concluded that the major structural differences between P-C Coke and normal furnace coke are :

1. Carbon Concentration - There is a higher concentration of carbon on a more continuous outside carbon surface of P-C Coke due to thicker cell walls caused by coalescence and inclusion of fine petroleum particles in the cell walls. (This is also confirmed by a 12.5 percent increase in apparent specific gravity of P-C Coke as compared to normal furnace coke.)
2. Internal Surface - There is a substantial reduction of internal surface area due to reduction of the number of fine pores.
3. Larger Pores - There are larger pores in P-C Coke due to coalescence of the plastic material from coals.

These enumerated P-C Coke characteristics enhanced the coke performance in the blast furnace test runs.

Before discussing the gasification characteristics of P-C Coke in relation to blast furnace conditions it may be well to enter into a brief review of the fundamental coke gasification concepts.

FUNDAMENTALS OF COKE GASIFICATION

Coke gasification has been studied extensively by a larger number of investigators over the years and reported in the literature. The accepted theory states gasification is a surface phenomenon which is greatly accelerated by temperature and retarded by surface films. The surface film which is the boundary between coke and oxidizing gases varies in thickness depending on the rate of coke gasification and disengagement of these gases. This is a dynamic balance and increased gas velocities passing over the coke reduce the film thickness. Diffusion through the surface film to the coke at high temperatures follows the mass law in that increase in available reactants results in increased rate of coke gasification in a given volume and thus higher temperatures result. This has been amply demonstrated in blast furnaces with oxygen enrichment of the blast. This same phenomenon occurs with a variation of apparent specific gravity of coke. Increased specific gravity results in more available carbon per unit surface under the film, as the carbon is more densely packed. In the past it has been demonstrated in the blast furnaces that higher temperatures and better driving rates were obtained when relatively light charcoal was replaced by heavier beehive coke and then again, when beehive coke was replaced by heavier high temperature by-product coke.

The work reported by Tu, et al., (13) sheds further light on the film diffusion theory of carbon combustion. Graph No. III summarizes some of the pertinent results showing variation of combustion rate with temperature, gas velocity oxygen concentration. He also shows that the rate of combustion varies linearly with percent oxygen up to 25 percent. At high temperatures where diffusion through the surface film is controlling, the rate of reaction varies as the 0.4 to 0.7 power of the mass velocity. In addition in this range, the rate of combustion varies approximately as the 0.6 to 1.1 power of the arithmetic mean temperature in degrees Kelvin. The work of Dubinsky (14) shows carbon gasification with carbon dioxide increases enormously in the temperature range of 1200 to 1400°C. In this range, temperature has relatively little effect on the rate of combustion for a given carbon in air.

Investigators have shown that coke gasification can be considered to occur in three steps, depending on temperature (8), (9), (15), (16). Graph No. IV, according to Wicke, illustrates this concept.

STEP I - At low temperatures, Step I occurs. In this range the rate of conversion of carbon dioxide to carbon monoxide is determined by total available surface carbon and the activation energy of coke. The total available (carbon) surface, includes both the external surface and internal pore surface which, for furnace coke, is in the range of two (2) square meters per gram.

From Graph IV it is noted that the rate of reaction increases rapidly with temperature in Step I.

STEP II - With increasing temperatures, the rate of increase of the reaction slows and a transition stage "a" is entered. Subsequently, Step II is reached in which the rate of reaction is so rapid that carbon dioxide, as it approaches the coke and its pores through the gas film, is in part converted and therefore the amount of carbon dioxide concentration reaching the internal pore surfaces of the coke is reduced.

This area, for convenience, can be referred to as pore diffusion zone. As a result less total effective surface becomes available for reaction and the rate of increase of the reaction is reduced to one half of that in Step I. The temperature range in which it occurs, by definition, is Step II.

STEP III - At further increasing temperatures, the rate of increase of the reaction slows and a transition stage "b" is entered. Subsequently, Step III is reached in which the rate of reaction is so high that no carbon dioxide is available for internal pore diffusion. In this area gas diffusion through the film is controlling. The diffusion coefficient is only slightly affected by temperature increases and therefore the rate of reaction increase is slowed down.

BLAST FURNACE CONDITIONS AFFECTING COKE GASIFICATION

An analysis was made of the fundamentals concerning blast furnace conditions and coke gasification to permit an explanation of the significant coke savings obtained with P-C Coke. A literature search revealed a considerable fund of information which must be carefully sifted to permit rationalization applicable to conditions existing in a blast furnace.

Of considerable interest on coke gasification is the work reported by B. Heynert and J. Williams (8), N. Peters and H. Echterhoff (9) and others (10), (11), (12). One of the main difficulties is to assess the relation of temperature in the blast furnace with gas composition. An approximation of this is possible with the sampling procedure used by Schurmann et al (10).

Graph II -A, based on work by Schurmann, shows the relation of temperature, with percent carbon monoxide, carbon dioxide, and total percent of carbon gases in a commercial blast furnace. The concentrations of carbon monoxide and dioxide, are strongly affected by temperature and the Boudouard reaction. From this Graph, it readily can be seen, that a desirable coke is one that will depress the reduction of carbon dioxide, to carbon monoxide. It is to be noted, that in the temperature

region where reactions of this type predominate, carbon dioxide is available from carbonate and iron oxide reduction in addition to that from carbon monoxide oxidation accompanied by carbon deposition. Therefore, a coke saving results with a coke which promotes increased concentration of carbon dioxide in the off gas, as it is more effectively used in oxygen removal.

The relation of temperature at various blast furnace elevations above the tuyeres, with percent carbon monoxide, carbon dioxide and the total percent of carbon gases, as reported by Heynert and co-workers, is shown in Graph II. Analyzing this curve from the point of view of carbon gases, four distinct zones are apparent.

ZONE I - The combustion zone in front of the tuyeres is considered as Zone I. In this zone for practical purposes no iron oxides are present and temperatures are at 3000°F and somewhat higher. Under these conditions the overall reaction of coke carbon with hot blast is :

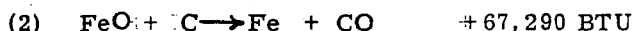


This reaction provides heat and reducing gases for iron ore reduction. High temperatures are developed which play an important role in hearth reactions. High temperatures result in hot metal with high silicon and low sulfur content due to the slag reactions. High temperatures, other conditions being equal, are the result of more carbon reaching the tuyeres and therefore the coke rate can be reduced to obtain comparable quality iron. If, however, the higher temperatures are also contributed to by the combustion characteristics of the coke then additional coke savings are possible by a stone saving to obtain comparable iron.

ZONE II - The area immediately above the combustion zone is characterized by the absence of carbon dioxide. This is due to the existing high temperatures at which carbon dioxide is unstable and, in the presence of carbon, decomposes to carbon monoxide. This area is the pure "direct reduction zone" in which the overall reaction of iron oxide is :



This reaction is pictured as going through the following mechanism :



Since reaction (2) consumes a considerable amount of heat the temperature drops rapidly in this area and as carbon monoxide is formed its concentration increases rapidly.

ZONE III - This area above the "direct reduction zone" is characterized by the appearance of stable carbon dioxide as temperatures have dropped sufficiently and a reduction of carbon monoxide occurs. The termination of this zone is the temperature range in which the Boudouard reaction reverses. To assist in showing

this the total carbon oxides are plotted on Graph II. Zone III can be referred to as "indirect reduction" zone. It is, of course, recognized that even though the direct reduction has been depressed some of it still proceeds. Besides this reaction a number of others occur with the end products consisting principally of Wustite, sponge iron, carbon monoxide and carbon dioxide.

The bulk of these reactions requires less heat than "direct reduction" and therefore the temperature drop in this zone is less until a point is reached where a strong endothermic reaction occurs. This area is where the main portion of the carbonates decompose and possibly other endothermic reactions occur. As there is an excess of carbon monoxide from Zone II for conversion of iron oxides to carbon dioxide, it is obvious that an unreactive coke, minimizing the reduction of carbon dioxide in Zone III, results in a coke rate reduction.

ZONE IV- Zone IV is characterized by the falling off of the total carbon oxide concentration and a rapid drop in ambient temperature. The total carbon oxide volume is reduced due to carbon deposition from the reaction of two volumes of carbon monoxide to one volume of carbon dioxide. The iron ore reduction reactions, similarly as in Zone III, proceed in this area with the modification that the end products favor carbon dioxide formation over carbon monoxide formation. The higher concentrations of carbon dioxide favor the oxidation of free metallics. Again in this zone it is obvious that a coke favoring the stabilization of carbon dioxide will result in a coke saving.

Inspecting the temperature profile on Graph II, it is noted that the carbon dioxide concentration is higher than predicted by the Boudouard equilibrium. This phenomenon is due to the fact that the temperature profile measures the ambient temperature while the Boudouard reaction is controlled by the reacting carbon surface temperature. This surface temperature is lower than the ambient temperature as strong endothermic reactions occur on its surface.

From the foregoing thermal and chemical considerations it was shown that a reduction in coke rate will occur in a blast furnace with a coke resulting in:

1. Increased temperature when gasified at the tuyeres.
2. Increased percent of coke gasifying at the tuyeres.
3. Reduced reaction rate with carbon dioxide to form carbon monoxide.

That an increase in the percent of coke gasified at the tuyeres results in coke saving was also demonstrated by M. Manes and J. S. Mackay (7). By means of a simplified mathematical model of a blast furnace, they showed that a coke rate reduction occurs with an increase in air per pound of coke charged with a concomitant reduction of air per unit of ore. They further deduced that "secondary reduction" (ore reduction below 1000°C) increased under these conditions.

DESIRABLE COKE CHARACTERISTICS

Considering the conditions affecting coke gasification in a blast furnace and the coke gasification fundamentals presented, it is apparent that a coke having the following characteristics will result in a coke rate reduction in a blast furnace:

1. Reduced Internal Surface

A coke with reduced internal surface will produce less carbon monoxide in the cooler upper portions of the stack and therefore a coke saving results. Further, a larger proportion will remain for gasification at the tuyeres and thus more heat is released in the hearth.

2. Increased Pore Diameter

A coke with increased pore diameters results in increased gasification with iron oxide in the pore diffusion range. This zone is significantly extended in a blast furnace from about 1000°C to as high as 1700°C due to the existing high gas velocities reducing surface film thickness. Therefore, a coke with large pores presents more available surface and gasifies more rapidly at temperatures existing in the direct reduction zone. The furnace level to which the direct reduction zone extends depends on temperature. As direct reduction consumes large amounts of heat, the acceleration of this reaction has a cooling effect and therefore the direct reduction zone stops at a lower level in the furnace.

3. Increased Carbon Concentration

A coke with higher concentration of carbon on its surface furnishes more reactants per unit area. Hence, at the tuyeres, the combustion temperature is increased as the reaction takes place in a smaller volume due to the mass action law. Consequently in the combustion zone, at equal total heat release, higher temperatures occur. Further it would appear that the carbon dioxide concentration becomes higher and also occurs at a point, closer to the tuyere nose. It may also be speculated that the higher temperatures occurring at the higher carbon dioxide concentration at localized areas in the combustion zone of the blast furnace contributes to the reduction of limestone usage (more acid slag) for proper metal quality control.

SUMMARY AND CONCLUSIONS

P-C Coke and H-C Coke, when used in blast furnaces, resulted in significant changes in operating results. These are summarized in Table V.

TABLE V.
EFFECT OF SPECIAL COKES VS NORMAL COKE IN BLAST FURNACES.

<u>OPERATING VARIABLES</u>	<u>P-C COKE</u>	<u>H-C COKE</u>
	<u>(85 Days)</u>	<u>(166 Hrs.)</u>
Burden Compared to Regular Practice	Normal	Variable
Coke Saving/THM, Pounds	100	87(a)
More Air/Pound Coke Charged, Cu. Ft.	1.8	-
Less Air/THM, Cu. Ft.	2820	6120
Less Blast Temp. Required °F	94	144
Stone Saving/THM, Pounds	58	138
(a) Corrected for burden variation.		

Inspection of the changes in operating results obtained with P-C Coke and H-C Coke clearly indicates that use of these special cokes effect a substantial coke saving as a result of reactivity characteristics differing from normal by-product furnace coke. In the case of P-C Coke, and by the indications obtained with H-C Coke, it was noted :

1. More air was required at the tuyeres per pound of coke charged, showing that a smaller proportion of coke is gasified in the stack and a larger proportion at the tuyeres.
2. Less air was required per ton of hot metal produced showing that the coke carbon was more effectively used with the oxygen from the ore.
3. Higher temperatures were experienced in the combustion zone as verified by a reduction in stone usage while producing comparable quality iron despite a reduction of both coke rate and blast temperature.

In view of the results obtained and the fundamental concepts presented, it was concluded that the reduced coke rate obtained with P-C Coke was caused by improved useful coke reactivity. This improvement was attributed to the following coke characteristics :

1. Less internal surface,
2. Larger pores,
3. Thicker cell walls.

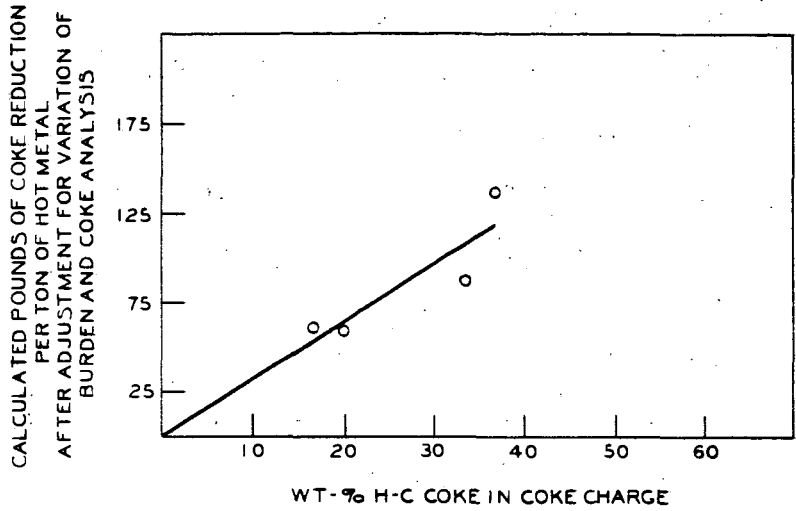
ACKNOWLEDGEMENT

This work could not have been accomplished without the active interest and efforts of J. D. Price, retired Coke Plant Superintendent, J. W. Carlson, Blast Furnace Superintendent, J. R. Purdy, Coke Plant Superintendent, and their staffs, all of The Colorado Fuel and Iron Corporation, and H. Loos, Works Manager, Hessische Berg U Huttenwerke AG, Oberscheld plant and his staff. Grateful thanks are extended to both these companies for permission to use data developed at their plants and to Professor T. L. Joseph for his many timely suggestions.

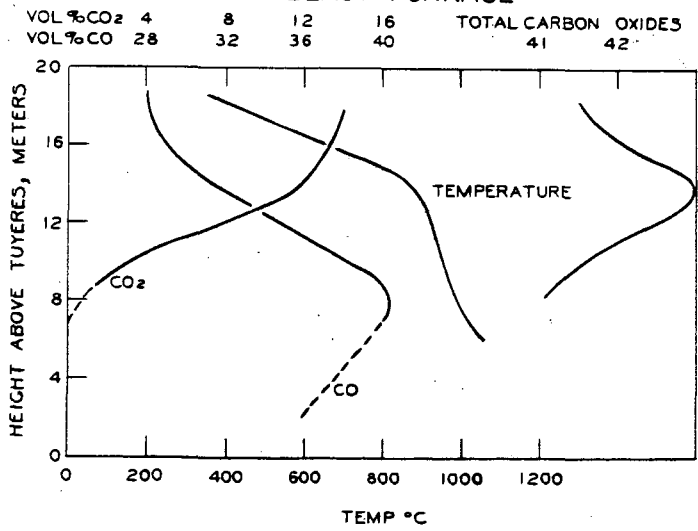
LITERATURE CITED

- (1) T. H. Blakley, J. W. Cobb, Inst. Gas Res. Fellowship Rept. 1931-1934 Com. No. 104
- (2) Broche and Nadelman Stahl U. Eisen, 53 (1953)
- (3) R. V. Flint, Blast Furnace & Coke Oven Proc. AIME (1952)
- (4) R. V. Flint, Blast Furnace & Steel Plt., 47-76, Jan. 1962
- (5) T. L. Joseph, Blast Furnace & Steel Plt., March & April 1961
- (6) M. A. Shapovalov, Stahl, H-5, 535-538, May 1958
- (7) M. Manes and J. S. Mackay, Jr. of Metals, April 1962, 308-314
- (8) G. Heynert and J. Williams, Stahl U. Eisen, 79, 1545-1554, (1958)
- (9) W. Peters, H. Echterhoff, Blast Furnace & Coke Oven Proc. AIME (1961)
- (10) E. Schurman, W. Zischkale, P. Ischebeck and G. Heynert, Stahl U Eisen 80, 845-861, (1960)
- (11) G. Heynert, W. Zischkale and E. Schurman, Stahl U Eisen, 80, 931-990, (1960)
- (12) G. Hedden, Lecture "Second European Simp. on Chem. Engr." Amsterdam (1960)
- (13) C. M. Tu, H. Davis, and H. C. Hottell; Ind. Engr. Chem., 26, 749-759 (1934)
- (14) M. S. Dubinsky, Thesis, Mass. Inst. Tech. (1932)
- (15) E. Wicke, K. Hedden, and M. Rossberg, Brenst. Warme Kraft 8, (1956)
- (16) G. Hedden, Chem. Ind-Techn., 30, 125-132, (1958)
- (17) B. Osann, Stahl U Eisen, 36 (1916) 477-434 and 530-536.

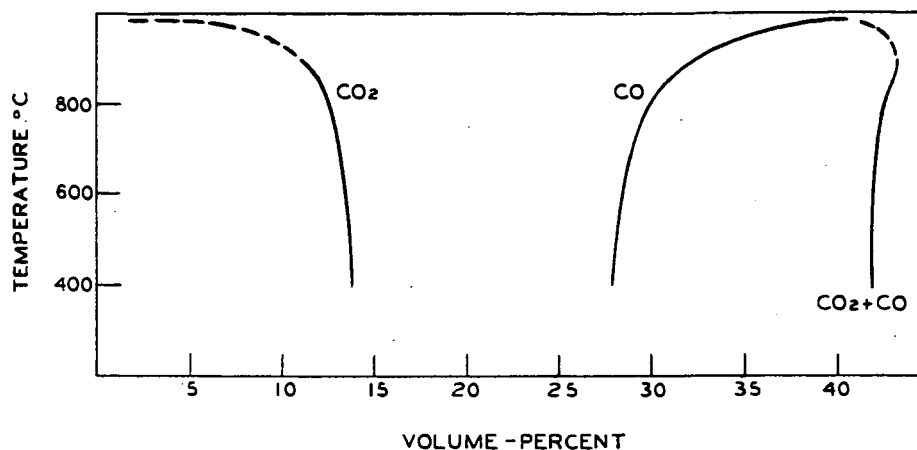
GRAPH I
COKE SAVING V S WT-% OF H-C COKE IN CHARGE



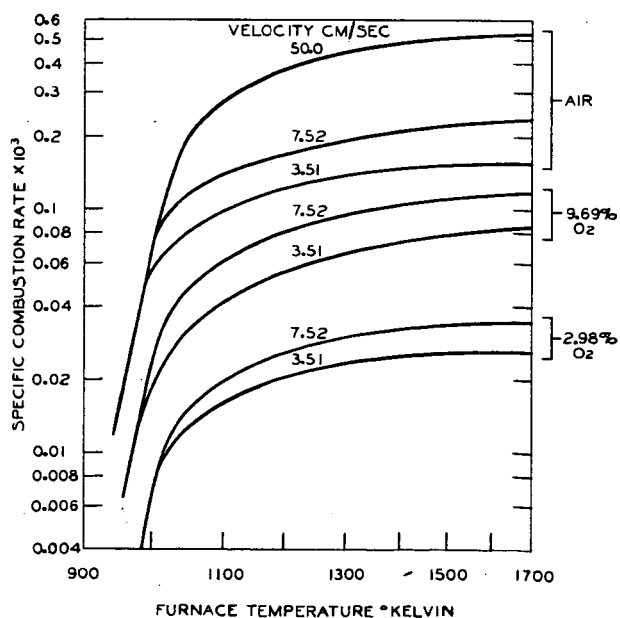
GRAPH II
PROFILE OF TEMPERATURE AND OXIDES OF CARBON
IN BLAST FURNACE



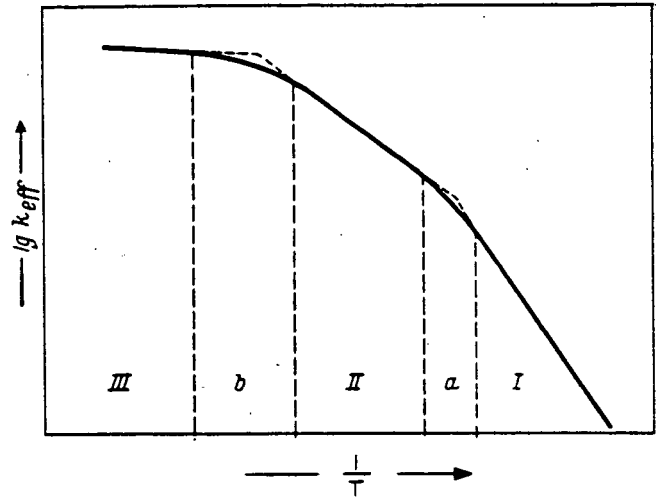
GRAPH II A
OXIDES OF CARBON AT VARIOUS TEMPERATURES



GRAPH III
RATE OF COKE COMBUSTION WITH GAS VELOCITY
AND OXYGEN CONCENTRATION



GRAPH IV
RATE OF GASIFICATION



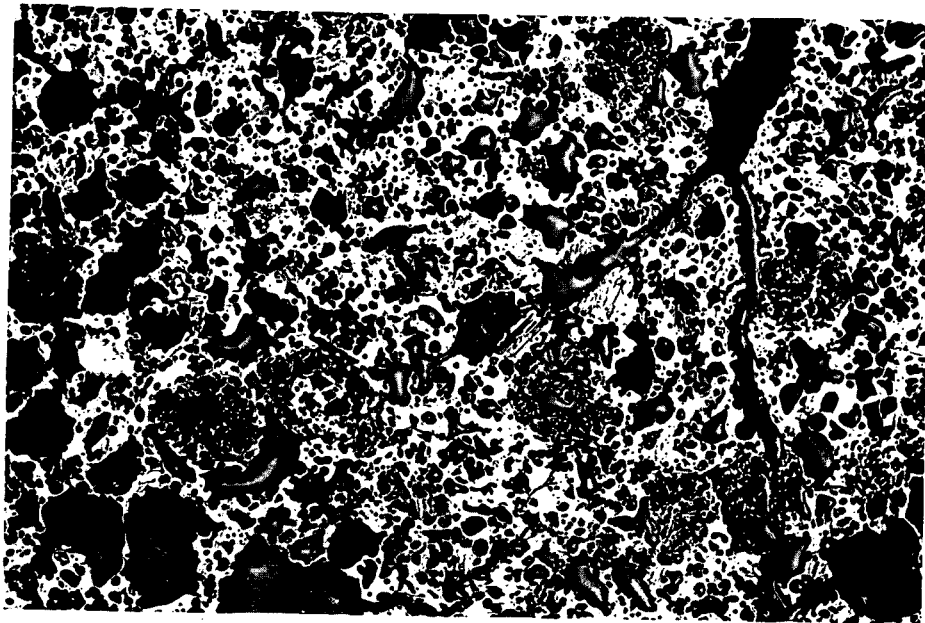


Fig. 1 CF&I NORMAL COKE, 10X

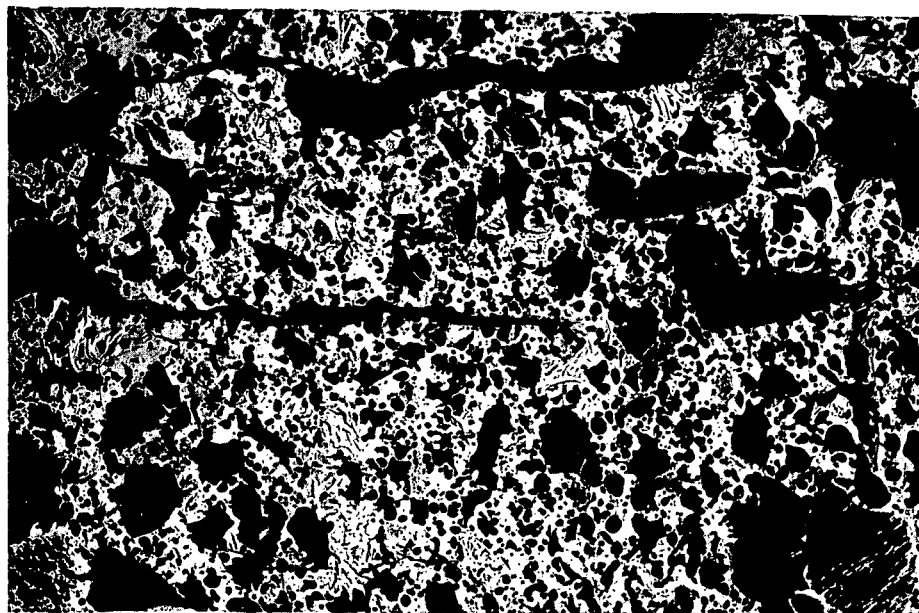


Fig. 2 CF&I P-C FURNACE COKE, 10X

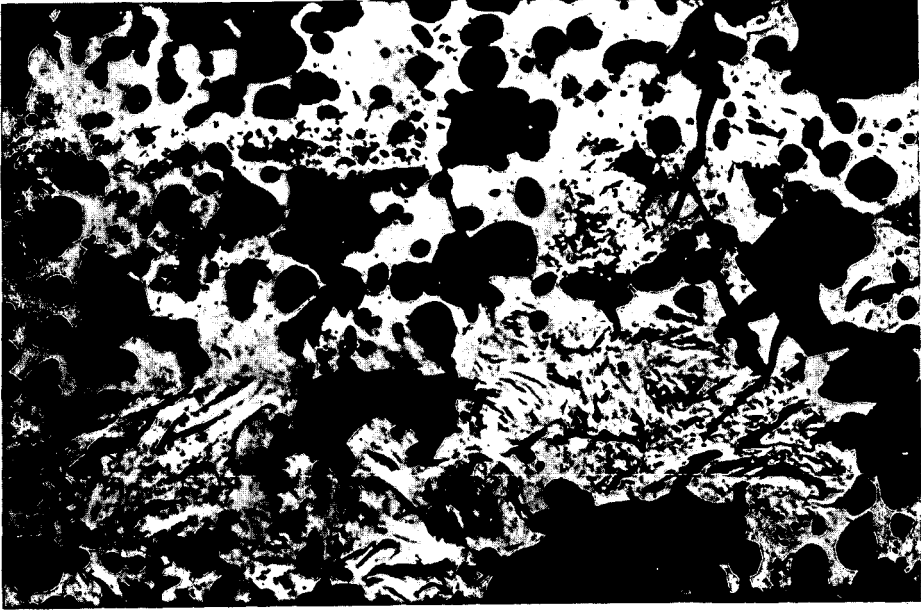


Fig. 3. CF&I P-C FURNACE COKE, 40X

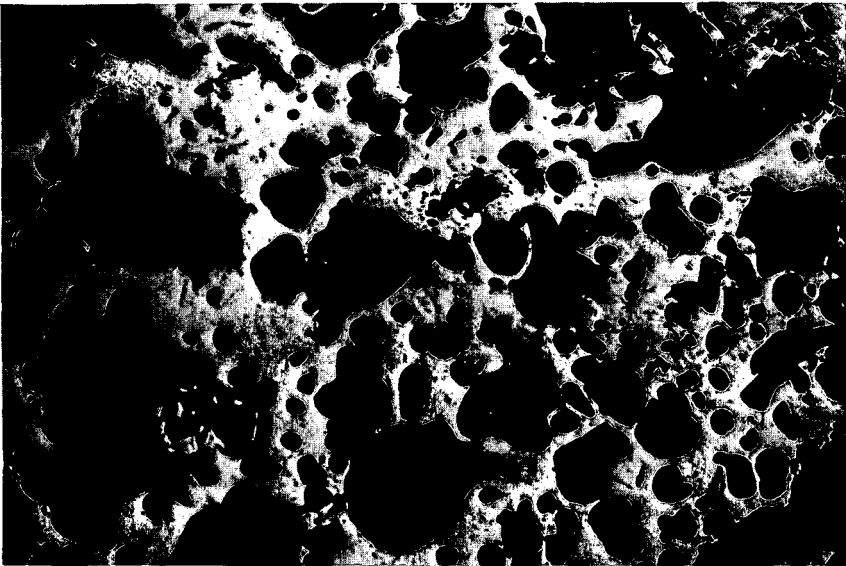


Fig. 4. CF&I NORMAL COKE, 40X

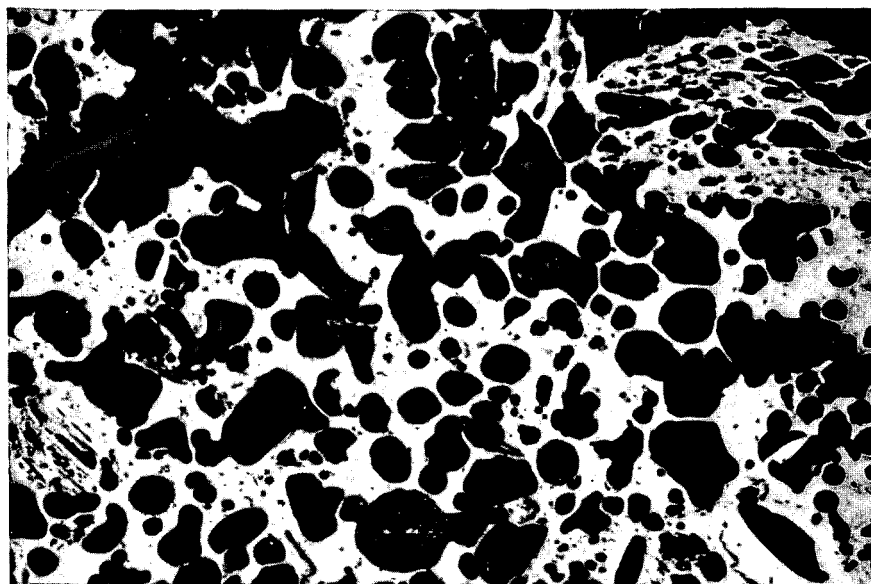


Fig. 5 COKE FROM 100% H. V. COAL, 40X

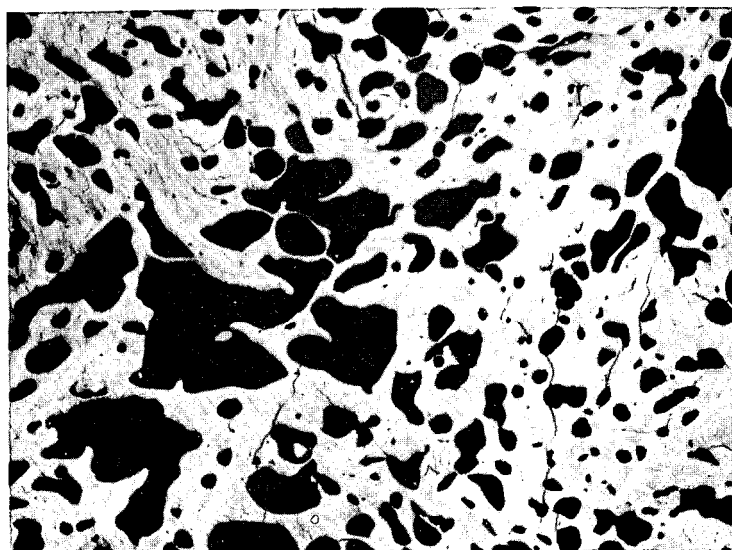


Fig. 6 RAW PETROLEUM COKE, 10X

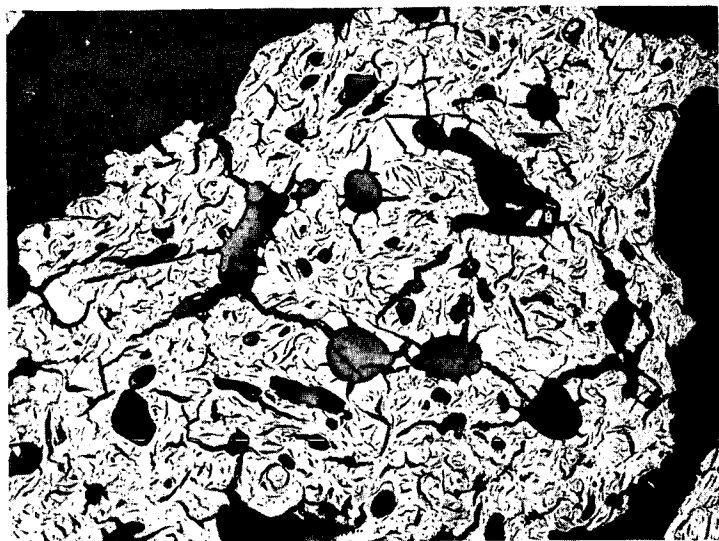


Fig. 7. CARBONIZED PETROLEUM COKE, 10X

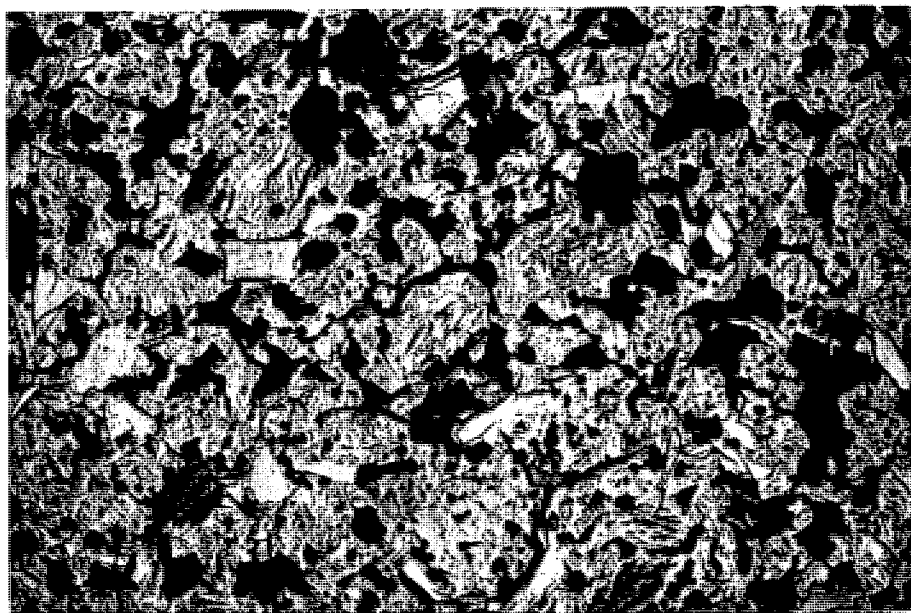


Fig. 8 DENSE FOUNDRY COKE, 10X